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A variational polaron self-interaction corrected total-energy functional for charge excitations in wide-bandgap insulators

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A simple modification of the density-functional theory (DFT) total energy functional is proposed that corrects for the polaron self-interaction error in semilocal approximations to the exchange-correlation potential. It can accurately reproduce polaron formation in wide-bandgap insulating materials. An extensive study of the potential energy landscapes of self-trapped holes in alkali halides is performed and agreeable comparison with hybrid DFT calculations and experiment is obtained. The new functional is general, simple to implement, and its variational formulation allows for *ab initio* molecular dynamics simulations of polarons in wide-bandgap insulators regardless of complexity.

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In wide-bandgap insulators charge excitations can couple to lattice distortions and thereby localize spatially. The quasi-particle resulting from this process known as a polaron is a single localized electron or hole dressed by a phonon cloud. In the limit where the coupling between charge excitations and phonons is strong one obtains small or Holstein polarons [1], characterized by large but localized ionic displacements. Small polarons are so strongly bound to the lattice that their dynamics can often be considered classical [2, 3]. Understanding their formation and transport thus calls for *ab initio* calculations of adiabatic, and sometimes diabatic [4], potential energy landscapes (PEL) of insulators containing charge excitations.

Small polarons appear in many technologically relevant materials including scintillators [5], batteries [6], and functional oxides [7]. Famously they appear in ionic crystals such as the alkali and earth alkali halides. In these systems hole carriers resulting from valence excitations open up the closed valence shells and allow for covalent bonding. As a result, a pair of nearest-neighbor halogen ions can dimerize and trap a hole leading to structures of the type shown in the inset of Fig. 1. The combined charge excitation (localized hole) and lattice distortion can be regarded as a point defect in the crystal lattice. In halides this hole polaron is commonly referred to as a V_K -center [8]. It is also known that in halides structure and transport of V_K -centers are related to those of self-trapped excitons [9]. Understanding the properties of polarons and self-trapped excitons is essential for modeling the microscopic processes associated with scintillation [10].

Density-functional theory (DFT) is a computationally efficient parameter-free methodology for calculating the chemical and electronic properties of materials from first principles. While it has been widely successful for many applications it qualitatively fails to describe polaron formation in wide-bandgap insulators both in the local density approximation (LDA) and the generalized gradient approximation (GGA) [11]. (Note that while LDA and GGA fail to predict the structural energies of polarons in normal insulators they offer accurate energies for the same systems when in their neutral

closed-shell states). By contrast, self-trapping and polaron formation are readily captured on the level of Hartree-Fock theory. The latter, however, delivers a poor description of the electronic structure of solids leading to largely overestimated band gaps and polaron formation energies. Hybrid techniques that combine semi-local exchange-correlation (XC) functionals with exact-exchange [12, 13] provide a bridge between the two techniques and constitute the state-of-the-art for studying various aspects of polarons in insulators, see e.g., [6, 11, 14]. The drawbacks of these hybrid methodologies are mainly twofold: (i) They are computationally very expensive, which limits their applicability to cases where the polaronic distortions are reasonably simple. In particular, exploring the mechanisms and rates for polaron transport using hybrid DFT functionals can be quite daunting. (ii) Hybrid DFT calculations are not parameter free. The fraction of exchange needs to be determined for a reference configuration and is then fixed through all configurational changes. This is justified as long as the overall electronic dielectric screening is not significantly altered.

Let us start by illustrating the failure of the DFT to predict polaron formation by quantifying its error for the prototypical V_K -center in NaI. In this system introduction of a hole in the valence band leads to a substantial lattice distortion, in which a pair of nearest-neighbor I^- ions move along $\langle 110 \rangle$ toward each other, reducing their distance from 4.5 Å in the perfect crystal to about 3.3 Å, effectively forming I_2^- . This distortion is accompanied by displacements of the surrounding atoms in order to accommodate the strain. Figure 1 shows the PEL along the pathway to hole self-trapping from DFT calculations based on the PBE XC functional [15], the PBE0 hybrid functional [12] as well as a modified PBE0-based hybrid functional (optimized hybrid), for which the fraction of exact-exchange is chosen to be 0.325 in order to reproduce the experimental band gap of NaI. Calculations were carried out using the project augmented wave method [16] as implemented in the Vienna *ab initio* simulation package [17] using a plane wave energy cutoff of 176 eV. We employed 216-atom supercells and the Brillouin zone was sampled using the Γ -

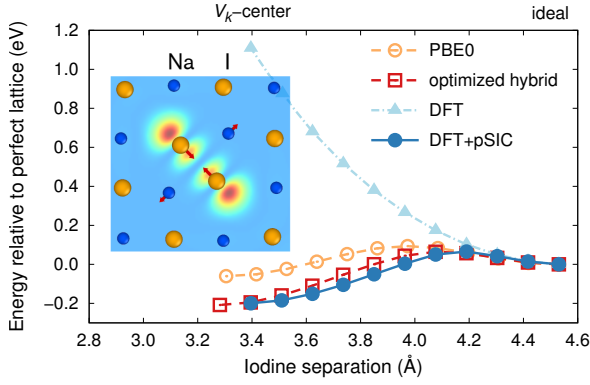


FIG. 1. Energy as a function of the two iodine ions that for the core of the V_K -center in NaI. The optimized hybrid has a mixing parameter of $\alpha = 0.325$ to be compared to $\alpha = 0.25$ for the PBE0 functional [12]. In agreement with the hybrid functionals DFT+pSIC calculations yield a stable polaron configuration while the DFT fails qualitatively.

point only. The comparison in Fig. 1 demonstrates that inclusion of exact-exchange is essential for capturing polaron formation in NaI. It is also evident that the polaron formation energy sensitively depends on the choice of the hybrid parameters as its value is reduced by a factor of two when the fraction of exact-exchange is changed from 0.325 (optimized hybrid) to 0.25 (PBE0). Note that in the absence of charge excitations, DFT predicts accurate structural energies, e.g. phonon spectra and defect formation energies.

There is little controversy to why DFT fails to stabilize small polarons in wide-bandgap insulators. While the self-interaction (SI) in LDA/GGA functionals leads to a large error in the description of localized polarons, the error is much smaller in the case of delocalized carriers. The introduction of explicit exchange largely corrects for the SI and allows for electron localization and polaron formation. The importance of SI was first discussed by Perdew and Zunger [18], who also proposed a one-electron approximation to the SI correction (SIC). This method greatly improves the description of atoms but has been less successful when applied to molecular structures and energies [19]. In recent years the SI error, in particular in finite systems with well-defined levels, has been discussed in terms of the deviation of the total energy functional from a piece-wise linear dependence on (fractional) level occupation with discontinuous derivatives at integer occupations [20–23]. It has been argued that optimal parametrizations of hybrid functionals should minimize this deviation [24]. In order to quantify this notion consider a many-electron system at a reference ground state with N_e^0 electrons. Let $E_{\text{DFT}}(\Delta)$ denote the total energy of this system as a function of the number of electrons Δ in excess of N_e^0 , calculated within DFT. Now we define $\Pi_{\text{DFT}}[\Delta]$ as the deviation of E_{DFT} from linear dependence around N_e^0

$$\Pi_{\text{DFT}}[\Delta] = \Delta \times \mu_{\text{DFT}}^{\pm} - (E_{\text{DFT}}[\Delta] - E_{\text{DFT}}[0]), \quad (1)$$

where $|\Delta| \leq 1$, and μ_{DFT}^+ (μ_{DFT}^-) is the right (left) derivative

of E_{DFT} with respect to electron number at N_e^0 for positive (negative) Δ . In an effort to go beyond the one-electron approximation to SIC, Dabo *et al.* [21] proposed a new class of SIC functionals by augmenting the DFT energy with approximate forms of Π_{DFT} . In practice, they used the deviation from piece-wise linearity of the band structure energy with respect to change of occupation of each single-particle orbital as their approximation to Π_{DFT} . This approach, quite like the Perdew-Zunger SIC, works well for atoms and may behave better for molecules but nevertheless both methods are difficult to implement in extended systems since they lead to orbital-dependent potentials that are not invariant under unitary transformations among the occupied orbitals [19, 25].

In the following, we formulate a new DFT-based energy functional that yields accurate polaron energies in wide-bandgap insulators by eliminating the polaron SI (pSI). Consider a system consisting of N_e^0 electrons and N_p ions. The ion positions are specified by the $3N_p$ -dimensional vector \mathbf{R} . The ground state energy of this system is described by $E_{\text{DFT}}[\Delta, \mathbf{R}]$, where Δ is the number of electrons in excess of N_e^0 . Using Eq. (1) we can express the total energy of the system with an electron added or removed from it as

$$E_{\text{DFT}}[\pm 1; \mathbf{R}] = E_{\text{DFT}}[0; \mathbf{R}] \pm \mu_{\text{DFT}}^{\pm}[\mathbf{R}] - \Pi_{\text{DFT}}[\pm 1; \mathbf{R}]. \quad (2)$$

We employ Π_{DFT} as a measure of pSI and formulate an energy functional that is free of this pSI. Note that in contrast to Dabo *et al.* [21] we do not resort to an approximate form of Π_{DFT} . Note, however, that the deviation from piece-wise linearity does not account for all the error in e.g., LDA or GGA. For illustration consider perfect crystalline systems such as Si or NaI. These systems are well described by the band picture and the delocalized carriers near the top (bottom) of the valence (conduction) bands have negligible $\Pi_{\text{DFT}}(\Delta)$. Nevertheless it is well-known that DFT fails to accurately predict ionization energies (μ^-) as well as electron affinities (μ^+) as manifested in the severe underestimation of band gaps by LDA/GGA. The band gap error originates from the absence of derivative discontinuities in LDA/GGA XC functionals [26, 27]. The correction to μ_{DFT}^{\pm} can be calculated for example by many-body perturbation theory within the GW formalism [28]. Finally, the energy functional for the system in excess of an electron/hole becomes

$$U^{\pm}[\mathbf{R}] = E_{\text{DFT}}[0; \mathbf{R}] \pm [\mu_{\text{DFT}}^{\pm}[\mathbf{R}] + \delta\Gamma_{\text{GW}}^{\pm}]. \quad (3)$$

Our goal is to use the above functional to perform structural relaxations of polaronic systems where DFT fails. The structure of the above equation is similar to Eq. (2). We have only replaced Π_{DFT} with the scissors shifts of the conduction/valence bands $\delta\Gamma_{\text{GW}}^{\pm}$. One necessary condition for Eq. (3) to be useful is that DFT accurately describes the structural energies of the reference system, i.e. $E_{\text{DFT}}[0; \mathbf{R}]$ is accurate. For normal insulators, this can be satisfied by choosing the reference system to be a closed-shell neutral insulator. The crucial approximation in Eq. (3) that makes it computationally feasible is the neglect of the \mathbf{R} -dependence of $\delta\Gamma_{\text{GW}}^{\pm}$,

which is to say we neglect the contribution of the scissors shift to the atomic forces. This is motivated by the work of Gygi and Baldereschi [29], who showed that due to the low excitation energies involved, $\delta\Gamma_{\text{GW}}^{\pm}$ is dominated by the long-range components of the static Coulomb hole plus screened exchange (COHSEX) contributions. Later it was shown that $\delta\Gamma_{\text{GW}}^{\pm} \approx \alpha^{\pm}/\varepsilon_{\infty}$ [30], where α^{\pm} and ε_{∞} (electronic dielectric constant) can be considered to vary weakly with localized lattice distortions, which is typical of polarons that preserve the structural long-range order as well as the insulating state. While this justifies the assumption of \mathbf{R} -independent $\delta\Gamma_{\text{GW}}^{\pm}$ above, it further implies that the accuracy of Eq. (3) can be improved by incorporating \mathbf{R} -dependence into $\delta\Gamma_{\text{GW}}^{\pm}$ through simplified COHSEX approximations without resorting to full-blown GW calculations.

Recently similar strategies to Eq. (3) were used to correct the DFT charged defect formation energies in semiconductors using full GW calculations for $\delta\Gamma_{\text{GW}}^{\pm}$ [31]. However, in these works all structural relaxations had to be performed strictly within DFT. Our aim here is to devise a robust method for structural relaxations/*ab initio* molecular dynamics simulations of polaronic systems that is easy to implement in existing DFT codes and is nearly as efficient as LDA/GGA. Equation (3) is not suitable for this purpose since μ_{DFT}^{\pm} is not a variational quantity and therefore its contribution to atomic forces cannot be evaluated using the Hellman-Feynman (HF) theorem. In the following, we show how this problem can be avoided. For this purpose we derive a total energy expression equivalent to Eq. (3) that is composed of individually variational components for which forces can be calculated using the HF theorem. Let us start by stating the desired form for such a total energy functional,

$$U^{\pm}[\mathbf{R}] = \sum_{n=0}^N w_n E_{\text{DFT}}[\pm\delta_n; \mathbf{R}]. \quad (4)$$

Above w_n are constant coefficients and δ_n are small charge increments. Note that every \mathbf{R} -dependent term in Eq. (4) is variational. The strategy is thus to replace μ_{DFT}^{\pm} in Eq. (3) with explicit numerical differentiation of the energy functional E_{DFT} with respect to the number of electrons. One then ends up with a weighted sum of $N + 1$ total energies at a number of fractional electron increments δ_n as in Eq. (4). In the simplest case we have $N = 1$ with $\delta_0 = 0$ and $|\delta_1| \ll 1$, which implies $w_1 = 1/\delta_1$ and $w_0 = 1 - 1/\delta_1$. Since δ_1 needs to be small in magnitude the weights w_n become large. This in turn requires the individual total energies to be converged with a very small residual error in order to obtain reasonably accurate values of U^{\pm} . This problem can be avoided by increasing the number of replica N . For the calculations presented in this paper, we have found that $N = 2$, with $\delta_n = 2.5 \times 10^{-3}n$ works well, and with individual total energies converged to better than 10^{-6} eV we have been able to perform structural relaxations to within 1 meV/Å in terms of residual forces. For $N > 1$ the coefficients w_n are calculated by minimizing the following functional with respect to the two variational pa-

rameters $U_0^+[\mathbf{R}]$ and $U_1^+[\mathbf{R}]$

$$\min_{\{U_0^+, U_1^+\}} \sum_{n=0}^N [E_{\text{DFT}}[\delta_n] - (U_0^+ + \delta_n U_1^+)]^2. \quad (5)$$

Note that for brevity we have omitted the dependence on \mathbf{R} in Eq. (5) and only consider positive charge increments. Minimization with respect to U_0^+ and U_1^+ leads to the following linear system of equations

$$\begin{pmatrix} N+1 & \sum_{n=1}^N \delta_n \\ \sum_{n=1}^N \delta_n & \sum_{n=1}^N \delta_n^2 \end{pmatrix} \begin{pmatrix} U_0^+ \\ U_1^+ \end{pmatrix} = \begin{pmatrix} \sum_{n=0}^N E_{\text{DFT}}[\delta_n] \\ \sum_{n=1}^N E_{\text{DFT}}[\delta_n] \delta_n \end{pmatrix} \quad (6)$$

By solving the above matrix equation and expressing the new total energy $U^{\pm}[\mathbf{R}]$ as

$$U^{\pm}[\mathbf{R}] = U_0^{\pm}[\mathbf{R}] + U_1^{\pm}[\mathbf{R}], \quad (7)$$

we can demonstrate that indeed as stated in Eq. (4), U^{\pm} can be written as a weighted sum of $N + 1$ variational total energies with the coefficients w_n having no dependence on \mathbf{R} . As a result the atomic forces can be calculated from the linear combination of separate HF forces following Eq. (4). We have implemented the energy functional Eq. (4) in the Vienna *ab initio* simulation package [17] allowing for the $N + 1$ replica to be run in parallel. The individually converged energies and forces are collected from all replicas and combined according to Eq. (4) after each ionic step.

Let us now review results obtained from the pSI-corrected (pSIC) energy functional applied to the PBE XC functional [15] using 216-atom supercells and a $3 \times 3 \times 3$ \mathbf{k} -point grid. Comparison to calculations that included only the Γ -point for sampling the Brillouin zone showed little change in the results. Revisiting Fig. 1 we see that in contrast to the DFT-PBE results, the new PBE-pSIC functional leads to a stable V_K -center configuration, whose geometry and energetics are in excellent agreement with the optimized hybrid functional. The bond-length of the I_2^- dimer that constitutes the core of the V_K -center is calculated to be 3.39 Å (3.30 Å) when using the pSIC (optimized hybrid) scheme while the energy gain due to self-trapping is found to be 0.24 eV (0.28 eV).

To further establish the accuracy of the pSIC method, we conducted an extensive comparison of its predictions with optimized hybrid functional calculations for the V_K -centers in alkali halides with rocksalt structure. These materials constitute a diverse class of wide-bandgap insulators with band gaps ranging between 5 to 13 eV and lattice constants from 4.0 to 7.3 Å. It is important to note that while the pSIC functional is parameter free, a range of mixing parameters for the exact-exchange must be used spanning from 0.28 for LiI to 0.45 for KBr in order for the hybrid method to reproduce the experimental band gaps. Figure 2(c) shows the dependence of the optimal mixing parameter on $\varepsilon_{\infty}^{-1}$ and verifies that a good choice for the optimal mixing parameter is typically close to $\varepsilon_{\infty}^{-1}$ [32, 33]. Figures 2(a) and (b) show comparisons of polaron formation energies [34] and geometries,

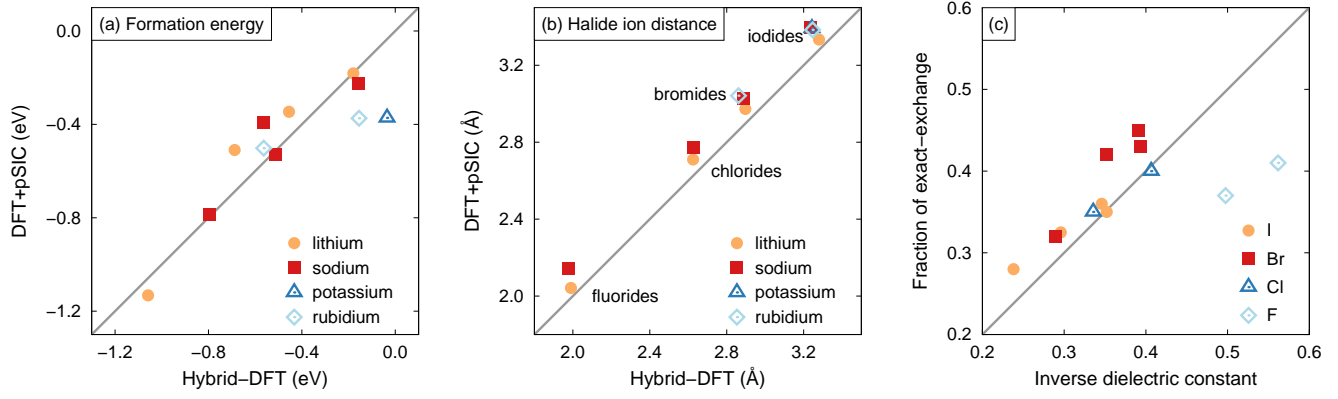


FIG. 2. Comparison of (a) V_K -center formation energies and (b) halogen-halogen separation at the core of the V_K -center between DFT+pSIC and hybrid DFT calculations. (c) Fraction of exact-exchange (mixing parameter of the hybrid functional) used for different halides to reproduce the experimental band gap as a functional of the latter as a function of the inverse electronic dielectric constant.

TABLE I. Activation barriers for polaron migration in units of eV from calculation and experiment.

Rotation Angle	Optimized hybrid	DFT+pSIC	Experiment
60°	0.25	0.197	0.2
90°	0.32	0.250	> 60°
120°	0.25	0.199	0.2
180°	0.28	0.186	

respectively, between optimized hybrid functionals and the pSIC functional for 12 compounds. The halogen dimer separation distances range from 2.0 Å to 3.4 Å, while the formation energies vary between -0.3 eV and -1.1 eV. Nevertheless, the agreement between optimized hybrid functionals and the pSIC-functional is astonishing. Also note that while corrections must be applied in the case of the hybrid calculations due to the long-range electrostatic interaction of polarons with their periodic images, the pSIC energies are free of such errors.

Up to now we have demonstrated that the pSIC functional is capable of quantitatively describing polaron formation in alkali halides without adjustable parameters. In order to further establish the validity of this approach, we have also calculated using the climbing image nudged elastic band method [35] the activation barriers for the four most plausible migration pathways of V_K -centers in NaI as shown in Table I. These migration pathways involve rotations of the halogen dimer through various angles commensurate with the symmetry of the rock-salt structure. We have chosen NaI since the polaron diffusivity has been quantified experimentally for this system [36]. To this end polarons were created and aligned along a particular direction (polarized) using a pump laser, after which their relaxation time for rotation was measured via a probe laser. Note that such experiments cannot measure the activation barrier for translation here referred to as the 180° pathway since it does not involve a change in polarization. For the same reason the experiments can also not distinguish between 60° and

120° rotations. At about 50 K almost exclusively 60°/120° rotations were observed, indicative of the fact that the activation barriers for these rotations must be significantly smaller than for 90° rotations. This result is confirmed by both optimized hybrid and pSIC calculations, see Table I. By fitting an Arrhenius curve to the temperature dependence of the rotational relaxation time in the experiments, one obtains an activation barrier for the 60°/120° rotations of about 0.2 eV. This is in almost perfect agreement with the pSIC result while the optimized hybrid calculations overestimate this barrier.

In conclusion, we have shown that the failure of DFT to describe polaron formation in wide-bandgap insulators is due to the self-interaction error associated with addition/removal of charge. We have devised a simple variational total energy functional, which implements an exact correction for this self-interaction error. There still remains an additional scissors correction that can in principle be obtained from G_0W_0 calculations. We then argued that for localized lattice distortions that do not significantly effect the overall electronic dielectric screening, the change in the scissors shift with atomic displacements can be neglected, and thus simple HF forces can be used to perform structural relaxations. This was demonstrated to be true by studying self-trapped hole formation and migration in the family of alkali halides using the new pSIC functional in comparison with hybrid functionals. It is observed that the parameter-free pSIC functional with a computational cost similar to the DFT, may at times be even superior in accuracy to the hybrid technique.

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